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(54) Process for the preparation of epoxides

(57) A process for the preparation of an epoxide from an olefin having a boiling point above 40°C at from 1 to 15 bar which comprises oxidizing acetaldehyde to peracetic acid using oxygen or a free oxygen-containing gas in an organic solvent and in the presence of a heavy metal oxidation catalyst and epoxidizing the olefin using the peracetic acid at a temperature of from 50 to 150°C at a pressure of up to 15 bar, the acetaldehyde, solvent and catalyst-containing peracetic acid reaction mixture obtained from the oxidation of the acetaldehyde being reacted with the olefin or a solution thereof in an organic solvent in the presence of a complex-forming agent and unreacted acetaldehyde, solvent and some of the acetic acid simultaneously being distilled off while a stream of inert gas is passed through the reaction mixture is disclosed.

The main advantage of the present process over the prior art is that it eliminates the dangerous purification by distillation of potentially explosive peracetic acid.

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SPECIFICATION

Process for the preparation of epoxides

5   This invention relates to a process for the prepara-
tion of epoxides; more particularly, it relates to a
process for the preparation of epoxides (oxiranes) by
the reaction of compounds having one or more
olefinic double bonds with peracetic acid.

10   Epoxidation using peracids has previously been
carried out by first preparing the percompound,
isolating and freeing it from reducing and decom-
posing substances, such as aldehydes and trace
heavy metals, by distillation, and finally reacting it

15 with the olefinic compound (see Ullmanns Encyk-
lopadie der technischen Chemie, 4th Edition, Vol-
ume 10, pages 563 et seq, Verlag Chemie,
Weinheim/Bergstr. 1975). The main disadvantage of
this process is that the isolation of the peracid in the

20 pure state entails the risk of explosion. The purifica-
tion of peracetic acid which has been prepared by
the oxidation of acetaldehyde using oxygen cannot
be omitted because unreacted acetaldehyde under-
goes a redox reaction with peracetic acid to form

25 acetic acid.
    A process which eliminates the dangerous purifi-
cation by distillation of peracetic acid has now been
found.
    The present invention relates to a process for the

30 preparation of an epoxide from an olefin having a
boiling point above 40°C at from 1 to 15 bar by the
oxidation of acetaldehyde to peracetic acid using
oxygen or a free oxygen-containing gas in an
organic solvent and in the presence of a heavy metal

35 oxidation catalyst, followed by epoxidation of the
olefin using peracetic acid at a temperature of from
50 to 150°C, optionally at a pressure of up to 15 bar.
The present process is characterised in that the
peracetic acid reaction mixture, which is obtained

40 from the oxidation of acetaldehyde and contains
acetaldehyde, solvent and catalyst, is reacted with
an olefin or a solution of an olefin in an organic sol-
vent in the presence of a complex-forming agent and
optionally an epoxidizing agent and at the same time

45 unreacted acetaldehyde, solvent and to some extent
acetic acid are distilled off while a stream of inert gas
is passed through.
    Accordingly, the present invention provides a pro-
cess for the preparation of an epoxide from an olefin

50 having a boiling point above 40°C at from 1 to 15 bar
which comprises oxidizing acetaldehyde to peracetic
acid using oxygen or a free oxygen-containing gas in
an organic solvent and in the presence of a heavy
metal oxidation catalyst and epoxidizing the olefin

55 using the peracetic acid at a temperature of from 50
to 150°C at a pressure of up to 15 bar, the acetal-
dehyde, solvent and catalyst-containing peracetic
acid reaction mixture obtained from the oxidation of
the acetaldehyde being reacted with the olefin or a

60 solution thereof in an organic solvent in the pres-
ence of a complex-forming agent and unreacted
acetaldehyde, solvent and some of the acetic acid
simultaneously being distilled off while a stream of
inert gas is passed through the reaction mixture.

65   In a preferred embodiment of the present process,

the peracetic acid reaction mixture is cooled to a
temperature of from −10 to +10°C, the complex-
forming agent and optionally the epoxidation catal-
yst are added to the peracetic acid reaction mixture

70 or to the olefin or olefin solution and the peracetic ·
acid reaction mixture is gradually added to the olefin
or olefin solution which is maintained under epoxi-
dation conditions.
    In another preferred embodiment of the present

75 process, the olefin or olefin solution and the perace-
tic acid reaction mixture are simultaneously con-
tinuously introduced into a reactor maintained under
epoxidation conditions, unreacted acetaldehyde,
solvent and some of the acetic acid being continu-

80 ously distilled off while an inert gas is passed
through and the epoxide-containing liquid reaction
mixture is continuously withdrawn from the sump of
the reactor.
    The first stage of the present process, i.e. the oxi-

85 dation of acetaldehyde to peracetic acid using
oxygen or a free oxygen-containing gases, such as
air, may be carried out by known methods in which
acetaldehyde diluted with a solvent is reacted with,
e.g., oxygen or air. Information on this step has been

90 given by D. Swern in Chemical Reviews, Volume 45 .
(1949), pages 5 to 8. In practice, the reaction is pref-
erably carried out in the presence of a catalyst.
Information on this may be found in, for example,
German Auslegeschrift No. 1,165,009.

95   Examples of suitable catalysts include: $FeCl_3$,
$Fe(NO_3)_2$, $Co(NO_3)_2$, $Co(CH_3COO)_2$ and molybdenum
acetonyl acetonate. The iron salts and cobalt salts
are virtually indistinguishable from each other in the
conversion rate produced and the selectivity. Gener-

100 ally the selectivity for peracetic acid formation is
over 90% and the aldehyde conversion ca. 60%.
    The catalyst may be used in the conventional
quantities, for example from 0.001 to 0.01%, by
weight, based on acetaldehyde.

105   Oxidation is generally carried out at the conven-
tional temperatures, for example from 0 to 30°C, pre-
ferably from 0 to 20°C. The reaction time is normally
from 30 to 120 minutes.
    Examples of the solvents which may be used for

110 the oxidation of acetaldehyde include: acetone, ethyl
acetate, chlorobenzene, methylethyl ketone, acetic
acid and methylene chloride; acetone and ethyl ace-
tate are preferred.
    The quantity of solvent used is generally chosen

115 so that the amount of acetaldehyde in the oxidation
mixture is from 5 to 40%, preferably from 10 to 20%.
    It is an essential feature of the present invention
that the reaction mixture obtained from the oxida-
tion of acetaldehyde is not worked-up to isolate pure

120 peracetic acid, but instead the reaction mixture con-
taining acetaldehyde, solvent and catalyst is reacted
with olefin. At the same time, most of the organic
solvent and some of the acetic acid formed, as well
as unreacted acetaldehyde, are continuously distil-

125 led off while an inert gas is passed through. This
may, of course, only be done if the boiling points of
the inert organic solvent and of acetaldehyde under
the conditions of epoxidation are lower than the boil-
ing point of the olefin used for epoxidation. The pro-

130 cess according to the present invention is therefore

only suitable for the reaction of those olefins which have a higher boiling point under the necessary conditions of epoxidation than that of acetaldehyde. The choice of a suitable inert organic solvent
5 depends, of course, on the boiling point of the olefin to be epoxidized, i.e. the boiling point of the organic solvent must be lower than the boiling point of the olefin under the conditions of epoxidation.

Examples of olefins which may be epoxidized by
10 the present process include: normal alkenes, iso-alkenes, substituted alkenes, oils, unsaturated fatty acids and polyolefins having double bonds in a mid-position and/or end position. The following may be mentioned as examples of such alkenes:
15 hexene-1, octene-1, decene-1, undecene-1, dodecene-1, octadecene-1, polycyclopentadiene, polybutadiene-1,2 and/or -1,4, allyl chloride, propylene trimer, linseed oil and oleic acid. All these olefins have boiling points above that of acetaldehyde.

20 Examples of olefins which cannot be used in the present process because the boiling point thereof is lower than that of acetaldehyde include ethylene; propene and the butenes.

Epoxidation is carried out at temperatures of from
25 50 to 150°C, preferably from 80 to 110°C, and at pressures of up to 15 bar. Epoxidation is generally carried out under pressure if a comparatively low boiling solvent is used, as is necessary if the olefinic compound which is to be epoxidized also has a rela-
30 tively low boiling point.

Examples of suitable solvents include: acetone, ethyl acetate, methylene chloride, methyl chloride, chlorobenzene and methylethyl ketone. For economical and technical reasons, the same solvent is used
35 for epoxidation as for oxidation of the acetaldehyde, preferably acetone or ethyl acetate.

Some possible and suitable process variables are exemplified in the following Table:

Alkene	Temperature (°C)	Pressure (bar)	Solvent
Hexene-1	90–100	12	Methylene chloride
Octene-1	90–100	3	Acetone
Decene-1	90–100	1	Ethyl acetate
Polybutadiene-1,2	90–100	1	"
Polybutadiene-1,4	90–100	1	"
Octadecene-1	90–100	1	"
Undecene-1	90–100	1	"
Propylene trimer	90–100	1	"
Oleic acid	90–100	1	"
Linseed oil	90–100	1	"
Allyl chloride	90–100	15	Methylene chloride

55 A complex-forming agent is used at the epoxidation stage to form a complex of the heavy metal catalysts used in the oxidation of aldehyde to peracetic acid and to prevent decomposition of the peracid by a reaction with metals of the wall of the
60 reactor (see M. Andoh et. al. Nippon Kagaku Kai Shi (1975) No. 8, 1383). Examples of suitable complex-formers include: polyphosphoric acid, pyromellitic acid and pyridine carboxylic acids.
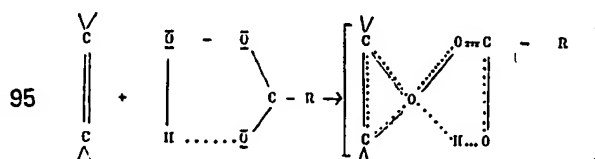
One of the conventional epoxidation catalysts may
65 be used is desired. These include, for example sulphuric acid, trifluoroacetic acid, tungstic and molybdic acids, alkane sulphonic acids, cation exchange resins and zinc phosphate. The complex-forming agents polyphosphoric acid and pyromelli-
70 tic acid also have a catalytic action on epoxidation.

The epoxidation catalysts or complex-forming agents are generally used in quantites of from 0.01 to 1%, by weight, preferable from 0.1 to 0.3%, by weight, based on the peracid.
75 It is preferred to use polyphosphoric acid or pyromellitic acid as complex-former and epoxidation catalyst during epoxidation or sulphuric acid as epoxidation catalyst and a pyridine carboxylic acid as complex-former.
80 In contrast to the known process, the catalyst used for the oxidation of acetaldehyde is left in the epoxidation reaction mixture. It has a decisive influence

on the course of epoxidation. It has been found that the selectivity of epoxidation is adversely influenced
85 by some of the catalysts used for the oxidation of acetaldehyde, for example inorganic catalysts which contain iron. This may be explained as follows: It is well known that a dicyclic addition complex corresponding to the following general formula is formed
90 as an intermediate product of epoxidation (see Bartlett. Rec. Chem. Proc., 11, 51 (1960):

The present investigations have shown that this
100 addition complex may decompose in two ways to form different reaction products:

only suitable for the reaction of those olefins which have a higher boiling point under the necessary conditions of epoxidation than that of acetaldehyde. The choice of a suitable inert organic solvent
5 depends, of course, on the boiling point of the olefin to be epoxidized, i.e. the boiling point of the organic solvent must be lower than the boiling point of the olefin under the conditions of epoxidation.
    Examples of olefins which may be epoxidized by
10 the present process include: normal alkenes, iso-alkenes, substituted alkenes, oils, unsaturated fatty acids and polyolefins having double bonds in a mid-position and/or end position. The following may be mentioned as examples of such alkenes:
15   hexene-1, octene-1, decene-1, undecene-1, dodecene-1, octadecene-1, polycyclopentadiene, polybutadiene-1,2 and/or -1,4, allyl chloride, prop-ylene trimer, linseed oil and oleic acid. All these ole-fins have boiling points above that of acetaldehyde.

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25 50 to 150°C, preferably from 80 to 110°C, and at pres-sures of up to 15 bar. Epoxidation is generally car-ried out under pressure if a comparatively low boil-ing solvent is used, as is necessary if the olefinic compound which is to be epoxidized also has a rela-
30 tively low boiling point.
    Examples of suitable solvents include: acetone, ethyl acetate, methylene chloride, methyl chloride, chlorobenzene and methylethyl ketone. For econom-ical and technical reasons, the same solvent is used
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	Decene-1	90–100	1	Ethyl acetate
	Polybutadiene-1,2	90–100	1	"
45	Polybutadiene-1,4	90–100	1	"
	Octadecene-1	90–100	1	"
	Undecene-1	90–100	1	"
	Propylene trimer	90–100	1	"
	Oleic acid	90–100	1	"
50	Linseed oil	90–100	1	"
	Allyl chloride	90–100	15	Methylene chloride

55   A complex-forming agent is used at the epoxida-tion stage to form a complex of the heavy metal catalysts used in the oxidation of aldehyde to peracetic acid and to prevent decomposition of the peracid by a reaction with metals of the wall of the
60 reactor (see M. Andoh et. al. Nippon Kagaku Kai Shi (1975) No. 8, 1383). Examples of suitable complex-formers include: polyphosphoric acid, pyromellitic acid and pyridine carboxylic acids.
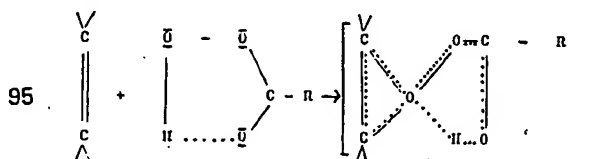   One of the conventional epoxidation catalysts may
65 be used is desired. These include, for example sul-phuric acid, trifluoroacetic acid, tungstic and molybdic acids, alkane sulphonic acids, cation exchange resins and zinc phosphate. The complex-forming agents polyphosphoric acid and pyromelli-
70 tic acid also have a catalytic action on epoxidation.
    The epoxidation catalysts or complex-forming agents are generally used in quantites of from 0.01 to 1%, by weight, preferable from 0.1 to 0.3%, by weight, based on the peracid.
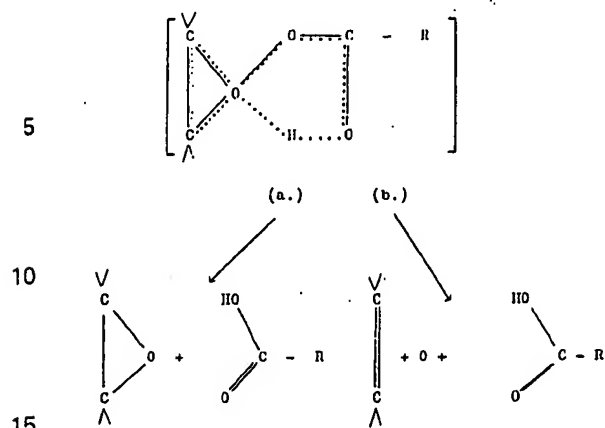75   It is preferred to use polyphosphoric acid or pyromellitic acid as complex-former and epoxida-tion catalyst during epoxidation or sulphuric acid as epoxidation catalyst and a pyridine carboxylic acid as complex-former.
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on the course of epoxidation. It has been found that the selectivity of epoxidation is adversely influenced
85 by some of the catalysts used for the oxidation of acetaldehyde, for example inorganic catalysts which contain iron. This may be explained as follows: It is well known that a dicyclic addition complex corres-ponding to the following general formula is formed
90 as an intermediate product of epoxidation (see Bart-lett. Rec. Chem. Proc., 11, 51 (1960):

    The present investigations have shown that this
100 addition complex may decompose in two ways to form different reaction products:

$$
\left[
\begin{array}{c}
\overset{V}{C} \quad O\text{----}C - R \\
\times \\
O \\
\underset{\Lambda}{C} \quad \cdots H \cdots O
\end{array}
\right]
$$

(a.)   (b.)

5

10

$$
\overset{V}{\underset{\Lambda}{C}}\!\!<\!\!O \;+\; HO\!-\!C\!-\!R \qquad \overset{V}{\underset{\Lambda}{C}} \;+\; O \;+\; HO\!-\!C\!-\!R
$$

15

Path (a.) represents the normal decomposition to the epoxide; path (b) is powerfully catalysed, e.g. by heavy metal ions, i.e. the reduction in selectivity is
20 due only to a minor extent to the direct decomposition of peracid since in the absence of olefinic double bonds the peracid is much more slowly decomposed by the presence of heavy metal ions under the same reaction conditions. Metals which are present in the
25 form of inorganic salts during the oxidation of acetaldehyde must therefore be rendered harmless by precipitation or complex formation. The above-mentioned compounds are examples of those suitable for this purpose.
30 Compared with the known process, the present process has the advantage that the distillation of peracetic acid, which entails the risk of explosion, and the stages of the process connected with this are omitted. Furthermore, in the present process the
35 amount of peracetic acid in the epoxidation reaction mixture may always be kept low and rapid reaction with the olefinic compound may nevertheless be achieved. Since in the present process most of the unreacted acetaldehyde is distilled off, virtually no
40 reaction takes place between the acetaldehyde and peracetic acid. This and the simultaneous removal by distillation of the solvents which are necessary for oxidation, but harmless for epoxidation enable a very high selectivity of epoxide compounds to be
45 achieved.

The following Examples illustrate the present invention:

Example 1

200 g of acetaldehyde and 1800 g of ethyl acetate
50 were introduced into an enamelled steel reactor equipped with a cooling jacket, a gas inlet, a gas outlet tube and a magnetic stirrer. 0.01%, by weight, of $FeCl_3$, based on the quantity of acetaldehyde, was added as catalyst. Oxygen was introduced for 2
55 hours at a pressure of ca. 4 bar and at the rate of 1 normal litre per hour into the mixture which was cooled to 10°C.

Analysis of the reaction mixture showed an aldehyde conversion of 63% and a peracetic acid
60 selectivity of 97%. The reaction mixture was used without any further working-up for the epoxidation described below.

For the epoxidation of decene-1, 100 g of decene-1 were introduced into a reaction tube (bubble col-
65 umn) and heated to 100°C by jacket heating. Nit-

rogen was then passed through the decene-1 at the rate of 20 litres per hour. 0.1 g of polyphosphoric acid was then added to 285 g of the reaction mixture containing peracetic acid which had been prepared
70 as described above and cooled to 0°C. This reaction mixture was then introduced into the heated reactor within 15 minutes. The reaction was continued for a further 5 minutes while a continuous stream of nitrogen was passed through. Most of the low boiling
75 constituents distilled off and were condensed in a condenser. The distillate still contained 29% of the peracetic acid put into the process, in addition to ethyl acetate, acetic acid and acetaldehyde.

An epoxidecane solution free from peracetic acid
80 was removed from the sump of the reactor and the solvent was distilled off. The conversion was 33%, based on decene-1, and 71%, based on peracetic acid. The selectivity based on epoxidecane, was 98% and, based on peracetic acid, 92%.
85 Example 2

A reaction tube equipped in its inner part with a steam heated coil having an inlet tube and gas outlet tube at its upper end and a gas inlet tube at its lower end and equipped in its outer part with a coil having
90 a gas inlet tube at its lower end and gas outlet tube at its upper end was used for the continuous production of epoxi-octadecane. The lower outlet tube of the inner coil opened into the lower part and the upper gas outlet tube of the inner coil into the upper
95 part of the outer part of the reactor.

A liquid reaction mixture consisting of 765 g of octadecene-1 and a reaction mixture containing peracetic acid as described in Example 1, to which polyphosphoric acid had been added, was intro-
100 duced at a temperature of 0°C into the upper inlet of the inner coil at the rate of 1540 g per hour. The reaction mixture containing peracetic acid consisted of 115 g of peracetic acid, 40.4 g of acetaldehyde, 2.8 g of acetic acid, 980 g of ethyl acetate, 0.1 g of $FeCl_3$
105 and 0.35 g of polyphosphoric acid.

The reaction mixtures flowed from above downwards through the steam heated coil and filled about 20% of its volume. A stream of inert gas was introduced at the lower end of the coil and carried in
110 counter-current to the reaction mixture. Most of the low boiling constituents (ethyl acetate, acetic acid, acetaldehyde and unreacted peracetic acid) evaporated and passed through the upper gas inlet tube into the upper space of the outer part of the reactor,
115 which functions as steam chamber of the after-reaction zone. The solution of epoxidecane free from peracetic acid passes through the lower outlet tube of the coil into the lower part of the outer reactor part which functions as after-reaction chamber. Inert gas
120 was also supplied to this part of the reactor. The remainder of the low boiling constituents evaporated there and were withdrawn from the upper part of the outer reactor part, together with the low boiling constituents evaporated in the coil, to be deli-
125 vered into a condenser by way of a cooler. The epoxidecane solution was drawn off the after-reaction chamber and then worked-up by distillation.

The conversion rate, based on octadecene-1, was 42%, and, based on peracetic acid, 92%. The selectiv-
130 ity, based on epoxioctadecane, was 97%, and, based

on peracetic acid, 90%.

CLAIMS

1. A process for the preparation of an epoxide
from an olefin having a boiling point above 40°C at
5   from 1 to 15 bar which comprises oxidizing acetal-
dehyde to peracetic acid using oxygen or a free
oxygen-containing gas in an organic solvent and in
the presence of a heavy metal oxidation catalyst and
epoxidizing the olefin using the peracetic acid at a
10 temperature of from 50 to 150°C at a pressure of up
to 15 bar, the acetaldehyde, solvent and catalyst-
containing peracetic acid reaction mixture obtained
from the oxidation of the acetaldehyde being reacted
with the olefin or a solution thereof in an organic
15 solvent in the presence of a complex-forming agent
and unreacted acetaldehyde, solvent and some of
the acetic acid simultaneously being distilled off
while a stream of inert gas is passed through the
reaction mixture.
20 2. A process as claimed in claim 1 in which an
epoxidation catalyst is used.

3. A process as claimed in claim 1 or claim 2 in
which the peracetic acid reaction mixture is cooled
to a temperature of from −10 to +10°C, the
25 complex-forming agent and any epoxidation catalyst
are added to the peracetic acid reaction mixture or to
the olefin or the solution thereof and the peracetic
acid reaction mixture is gradually added to the olefin
or solution thereof which is maintained under epox-
30 idation conditions.

4. A process as claimed in any of claims 1 to 3 in
which the olefin or the solution thereof and the
peracetic acid reaction mixture are simultaneously
continuously introduced into a reactor maintained
35 under epoxidation conditions and the epoxide-
containing liquid reaction mixture is continuously
withdrawn from the sump of the reactor.

5. A process as claimed in any of claims 1 to 4, in
which acetone or ethyl acetate is used as solvent for
40 the oxidation and the epoxidation.

6. A process as claimed in any of claims 1 to 5 in
which polyphosphoric acid or pyromellitic acid is
used as complex-forming agent and epoxidation
catalyst.

45 7. A process as claimed in any of claims 1 to 5 in
which sulphuric acid is used as epoxidation catalyst
and a pyridine carboxylic acid is used as complex-
forming agent.

8. A process as claimed in claim 1 substantially
50 as herein described.

9. A process as claimed in claim 1 substantially
as herein described with reference to Example 1 or
Example 2.

10. An epoxide when prepared by a process as
55 claimed in any of claims 1 to 9.